BENNETT

Experiments on the Assay of Copper Mattes and Ores

Chemical Engineering

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EXPERIMENTS
ON THE
ASSAY OF COPPER MATTES AND ORES

BY

ARTHUR NORTON BENNETT

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

COLLEGE OF SCIENCE

UNIVERSITY OF ILLINOIS

PRESENTED JUNE, 1907

1907
B43

UNIVERSITY OF ILLINOIS

May 31 1907.

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Arthur Norton Bennett

ENTITLED Experiments on the Assay of Copper Mattes and Ores.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science

in Chemical Engineering.

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EXPERIMENTS ON THE ASSAY OF COPPER MATTES AND ORES.

Outline.

I. a. Introduction and historical.
   - b. Object.
   - c. Reagents used.

II. Experimental.
   - a. Experiments with copper matte by combination method.
   - b. Experiments with copper matte by all-fire method.
   - c. Experiments with copper matte by nail method.
     - 1. Experiments with C. P. silver.
   - d. Experiments with copper matte by nitre method.
   - e. Experiments with copper matte using nitre and sodium peroxide.
   - f. Experiments with copper matte using lead peroxide and red lead.
   - g. Determination of the copper slagged in the foregoing experiments.
   - h. Comparison of results.
   - i. Experiments with copper ore.
   - j. Experiments to determine the influence of litharge on the slagging of copper.

III. Conclusion.

IV. Bibliography.

I. a. Introduction.

The assay of copper-ores,-- matte and bars which contain gold and silver has been the subject of much discussion. The methods now in use are long and difficult to carry out successfully without considerable experience. Moreover they give such a variety of results that the assayer is enabled to obtain either a high or low result by judicious choice of his method. Thus one can obtain almost any result desired depending on his being a buyer or seller. This practice has gone so far in England that they have there two separate classes of assayers, the 'buyer' assayer and the 'seller' assayer. To improve these conditions, the more conscientious chemists have for many years been endeavoring to establish some uniform method or methods for the assay of gold and silver bearing copper materials, similar to the international standards for the analysis of iron and steel.

With this end in view A. R. Ledoux[1] in 1894 proposed and started a plan of co-operative action for the members of The American Institute of Mining Engineers. His plan was as follows. Each assayer who was willing to join in the 'symposium' was to be supplied witha number of samples

of gold and silver bearing copper materials. These samples were to be assayed by the standard methods in use in that particular laboratory and the results with a detailed description of the methods were to be sent to the secretary of the Institute to be published by him without the names of the assayers or works. By a general discussion of the results published it was hoped to obtain some uniform method. This plan of Mr. Ledoux met with considerable success and while it did not attain the end hoped for, it did a great deal towards bringing about a universal discussion of the subject. Mr. Ledoux[1] himself proposes the following methods which he claims can be quite generally used for assaying copper borings and mattes.

For Gold. One assay ton of the material is treated in a No. 5 beaker with a mixture of 100 c. c. water and 50 c. c. nitric acid of sp. gr. 1.42. When the violent action has ceased 50 c. c. more of the nitric acid are added and the solution gently heated until all soluble material has been dissolved. The solution is then diluted to about 400 c. c. and 5 c. c. of concentrated sulphuric acid is added and then 10 c. c. of a concentrated solution of either lead acetate or nitrate. The lead sulphate which acts as a collector of the

gold is allowed to settle for some hours. It is then filtered off and washed free from copper. The filter is partially dried, wrapped in thin lead foil and scorified with 50 grams of test lead. The resulting button is then cupelled in the usual way.

For Silver. The method is the same as for gold except that after the addition of the sulphuric acid and before the lead salt is added, enough sodium chloride solution is added to precipitate all the silver present. From this point the method of procedure is the same as for gold.

These methods somewhat modified in the different laboratories are in general use throughout the East.

L. D. Godshall[3], Cabell Whitehead[4], [9], W.R. Van Liew[6], T. B. Swift[7] and many others have perfected modifications of the combination method, all of which give good results in the hands of an experienced assayer.

L. D. Godshall's[3] method is worthy of a brief description as it is quite different from that described above.

The material is dissolved in dilute nitric acid and a small amount of concentrated sulphuric acid is added. The excess of nitric acid is driven off and the residue is taken up with water. Then hydrogen sulphide is passed through the

solution until all the silver and a small amount of copper, which can be reduced to a minimum with a little practice, is precipitated. The sulphides are filtered off, dried, scorified, and cupelled.

In the West the all-fire method is used almost exclusively. In the Omaha and Grant works the following method[1] is used. Ten portions of the sample of 0.1 A. T. each are scorified with 50 grams of test lead and about 1 gram of borax. The lead buttons thus obtained are cupelled separately but the ten beads are weighed together. The cupels used are ground up and fused in five lots of two each with the following charge:-- litharge, 90 grams; soda, 50 grams; borax-glass, 50 grams; and argols, 3 grams. The five buttons are cupelled and the silver is added to that obtained in the first operation. All the beads are then parted for gold. This method has the advantage of obtaining both metals at the same time and it agrees very well with the combination process for silver but as a rule gives higher results for gold as may be seen by the following table which very well illustrates the need of some international standard method.

Gold in ounces per ton.

	All-fire method.	Combination method.
1.	1.06	.92
2.	1.32	1.24
3.	2.76	2.56
4.	2.72	2.44

For a detailed description of the various methods brought out by Mr. Ledoux "symposium," the reader is referred to the "Transactions of the American Institute of Mining Engineers" 25, 250, 1895.

One method for the assay of metallic copper is worthy of mention since it has a bearing on certain of the experiments to be described later. This method was perfected by G. L. Heath[2] and A. S. Warren. In brief it is as follows. The Copper borings are dissolved in nitric acid; the solution is diluted and the silver precipitated with a sodium chloride solution. The silver chloride is filtered off and washed free from copper. From 1.5 to 2 grams of test lead are sprinkled over the chloride and the filter still wet is folded down and placed in a red hot cupel to which 4 or 5 grams of test lead has just been added. The cupel is shoved back into the hottest part

of the muffle and by the time the filter is burned off the silver chloride has all been reduced.

b. Object.

These experiments were undertaken primarily for the purpose of obtaining a shorter method for the assay of gold and silver bearing copper materials, one which should also compare favorably with the methods now in use. A secondary object of the investigation was the use of sodium peroxide as a flux and oxidizing agent in the assay of copper materials.

c. Reagents used.

The litharge used in all these experiments was assayed for gold and silver, the following charge being used.

Experiment 1.	Experiment 2.
Litharge 120 grams	Duplicate.
Soda Carbonate 20 grams.	-----
Borax glass 10 grams.	-----
Argols 3 1/2 grams.	-----
Wt. of Au plus Ag .00055 grs.	.00053 grams.

The test lead used gave not even a trace of silver when a 150 gram sample was run by scorification.

The sodium peroxide used was analyzed by Mr. A. Scholz and found to be about 95 per cent pure.

II. Experimental.

a. Assay of Copper by the Combination Wet and Dry Method.

The copper matte (ore No. 10) used in this experiment and in all subsequent experiments in which a matte is used was analyzed by the iodide method[10] and found to contain 56.01 per cent Cu. It was ground to pass through a 100 mesh sieve and was well mixed and sampled before using.

The following method was used for determining the silver in the matte. Three samples, Nos. 3, 4, and 5 respectively, of 1 A. T. each were treated in five inch casseroles with 100 c. c. of water and 50 c. c. of nitric acid of sp. gr. 142. The nitric acid was added slowly to avoid too violent action. After all the acid had been added the solution was boiled for about ten minutes by which time the matte was entirely decomposed. The solution was allowed to cool and was then diluted to about 400 c. c. Three c. c. of N

NaCl solution were then added and the whole stirred vigorously for a few minutes. The solution was allowed to settle over night and filtered through two 15 cm. Swedish filters and washed with cold water acidulated with nitric acid. The filters, which were still wet, were placed in 3 1/2 inch scorifiers containing 6 grams of test lead and were ashed in front of a muffle which had not yet reached a red heat. When completely ashed 40 grams of test lead were added to the residue and thoroughly mixed with it. This mixture was then covered with 40 grams more of test lead and scorified after adding a pinch of borax glass and about 1 gram of silica. The scorification was carried on at as low a temperature as possible and gave a good clear pour, the slag giving no indication of the presence of copper. The resulting buttons were too large for cupellation so enough test lead was added to bring the total up to 50 grams and the buttons rescorified. The buttoms from this second scorification were then cupelled at a temperature which gave litharge crystals.

Results.

	Experiment No. 3.	No. 4.	No. 5.
Weight of lead for cupellation	12 grs.	13.5 grs.	10.5 grs.
Ounces of Ag per ton	105.57	106.03	106.03

No. 3 sprouted while cooling and also left one or two

minute globules of silver on the cupel; hence the low result. The value 106.03 ounces per ton was taken as the correct result and was used as a check in all subsequent experiments.

b. Copper Matte by Scorification Method.

Four samples of 0.1 A. T. each were taken and scorified with 70 grams of test lead, mixing one half of the lead with the matte and using the other half as a cover. It was found necessary on account of the amount of copper in the resulting button, as shown by their hardness, to make two rescorifications. Each time enough test lead was added to the button to bring the total weight to 50 grams. The results obtained by this method were considerably lower than those from the combination method. This was probably due to the scorification losses. No attempt was made to determine directly the amount of silver lost in this way.

Results.

Experiment	No. 6.	No. 7.	No. 8.	No. 9.
Wt. of lead for cupellation	18 grs.	20 grs.	20 grs.	20 grs.
Wt. of silver	.00960 "	.00999"	.00994 "	.00988 grs.
Ounces of silver per ton	96.0	99.9	99.4	98.8

c. Assay of Copper Matte by the Nail Method.

The methods used in the two preceding experiments are modifications of the ones now in general use and the results obtained were used for comparison with the results of subsequent experiments in which new methods were used. The old combination method while it gives very good results takes at least twenty four hours for the completion of an assay, while with the all-fire method it is impossible to remove all the copper from the lead button and consequently a higher heat is necessitated for cupellation. This together with the absorption by the cupel of some of the silver with the copper causes a considerable loss.

In the combination method described above the matte is treated with nitric acid for the purpose of dissolving the copper. Aside from the fact that some copper bearing substances require long boiling with acid before they are completely decomposed, there is also the disadvantage that a residue is left which must be scorified. It was thought possible to shorten the usual method by making a fusion in which the silver would be collected in a lead button together with any copper that was reduced. This button could then be dissolved in nitric acid, the silver precipitated as the chloride, filtered and cupelled direct. To test this method the following

experiments were made.

The button was flattened on the anvil and broken into pieces to aid solution. It was then dissolved in the least possible amount of nitric acid, and the solution diluted to about 350 c. c. Three c. c. of a N NaCl solution were then added and after stirring for several minutes the silver chloride was allowed to settle. If the solution is stirred by means of compressed air for about one half hour, it can then be immediately filtered. The silver chloride was filtered on a 9 cm. filter with the aid of suction. After washing out all the copper with cold water acidulated with nitric acid, the filter was dried and then ashed over a two inch square of lead foil which contained from 5 to 10 grams of test lead. The silver chloride and ash were mixed with the test lead, wrapped in the lead foil and cupelled at as low a heat as possible. In this particular series of experiments the fusions were made according to the method given by Lodge8 in his 'Notes on Assaying.' The charges used and the results obtained were as follows.

	Experiment No. 10.	No. 11.	No. 12.
Matte used	.5 A. T.	Duplicate	Duplicate
Soda carbonate	40 grams		
Borax	12		
Litharge	20		
Nails 20 d	4		
Silica	8		
Salt	Cover		
Wt. of lead button	27.3	27.3	30.3
For cupellation	14	19.5	29
Wt. of Ag	.04908	.05100	.04620
Correction	.00009	.00009	.00009
Oz. of Ag per ton	97.98	101.82	92.22

These fusions and all subsequent ones in this series poured well and gave a hard, black, basic iron slag which was free from globules of lead. The buttons from Nos. 10 and No. 11 were treated with 70 c. c. of nitric acid of sp. gr. 1.42 and 150 c. c. of water. Solution was complete in about twenty minutes. The filters containing the silver chloride obtained as described above were moistened with ethyl alcohol and ignited without drying. It was found later to be more satisfactory and nearly as rapid to dry the filters and ignite them without the use of alcohol.

	Experiment No. 13.	No. 14.	No. 15.
Matte taken	1 A. T.	.5 A. T.	1 A. T.
Soda carbonate	100	50	90
Borax	20	12	12
Litharge	20	20	20
Nails 20 d	4	4	4
Silica	12	2	20
Cover	Salt	Salt	Borax
Wt. of lead	39	28.5	39.5
Wt. of lead for cupellation	24	20	20
Wt. of Ag	.10021	.04801	102.60
Correction	.00009	.00009	.00009
Ounces of Ag per ton	100.12	95.84	102.51

As seen from the above tables the results obtained by this method are considerably lower than those obtained from the combination method. Consequently the following experiments No. 16, No. 17, No. 18, and No. 19 were carried out to determine whether the low results were due to volatilization of a part of the silver by the sodium chloride used to cover the charge, and also to show whether or not there was a greater loss of silver due to the volatilization of silver chloride when cupelled direct than when it is first reduced by means of a scorification. The filters containing the silver chloride were placed in

2 1/2 inch scorifiers and ashed in front of a muffle heated to a dull red. The residue was then scorified with 50 grams of test lead and the resulting button cupelled as usual.

Results.

Experiments	No. 16.	No. 17.	No. 18.	No. 19.
Matte used	1 A. T.	1 A. T.	1 A. T.	1 A. T.
Soda Carbonate	90 grs.	90 grs.	90 grs.	90 grs.
Borax	10	10	20	20
Litharge	20	20	20	20
Nails 20 d	4	4	4	4
Silica	20	20	15	15
Cover	Borax	Borax	Salt	Salt
Wt. of lead	40	41	41	40
Wt. of lead for cupellation	20	20	20	20
Wt. of Ag	.10262	.10210	.10216	.10116
Correction	.00009	.00009	.00009	.00009
Ounces of Ag per ton	102.53	102.01	102.07	101.07

Experiments No. 18 and No. 19 in which salt is used as a cover gave practically the same results as No. 16 and No. 17 in which borax was used as a cover. Also a comparison with the result obtained in Experiment No. 15 in which the silver chloride was cupelled direct and which gave 102.51 ounces of

Ag per ton will show that there is no more loss by direct cupellation than there is by a preliminary scorification and subsequent cupellation.

The foregoing results show that while this method does not give as high results as the combination wet method, it is more satisfactory than the scorification method. It gives higher results and takes less time.

It is well known, however, that in the assay of mattes containing large amounts of silver (400 to 500 ozs. per ton) the direct cupellation of the silver chloride is attended with considerable loss. Consequently the method of cupellation would have to be modified in using the above method for the assay of rich mattes.

The following experiments were undertaken with the object of determining the loss of silver chloride in direct cupellation and also to find a method to prevent this loss by adding to the precipitate substances which would break up the silver chloride before it could volatilize.

To determine the loss of silver caused by direct cupellation of the chloride as described above, the following experiments were made.

Experiment No. 20. Three samples of c. p. silver

weighing about 0.4 gram each were dissolved in 2 c. c. of nitric acid of sp. gr. 1.42 and about 5 c. c. of water. The solution was diluted to 200 c. c. and heated to about 60° C. Six c. c. of a N NaCl solution were then added and the solution stirred until the precipitated chloride collected in a curdy mass. After standing for several hours the precipitate was filtered off on a 9 cm. filter and washed with water acidulated with nitric acid. The filter was then dried and ashed and the residue cupelled with test lead and lead foil as described above. At thesame time two other samples of c. p. silver of the same weight as the others were cupelled direct with 15 grams of test lead and lead foil. These two determinations gave the loss due to cupel absorption and volatilization of the silver itself and served as checks for the other determinations. The check samples gave a loss of 1.87 per cent and 1.88 per cent while in the direct cupellation of the silver chloride there were losses of 2.42 per cent; 9.22 per cent and 7.90 per cent respectively. From the result of the determination in which there was a loss of only 2.42 per cent it would seem that there are certain conditions under which this method would give a very slight loss but as shown by the other two results these conditions are hard to obtain for all three determinations were seemingly

treated in the same way.

Experiment No. 21. This series was carried out for the purpose of finding some substance which when added to the precipitate would prevent volatilization by decomposing or reducing the silver chloride. Seven samples of c. p. silver weighing from .35 gram to .39 gram were treated as described under experiment No. 20 up to the point where the silver chloride is obtained on the filter. From there on the different determinations were treated as follows. In two of the determinations powdered charcoal was well mixed with the silver chloride after the filter had been ignited. These cupelled well but gave a rather high loss, 2.84 per cent and 3.33 per cent respectively.

Two other determinations were treated in the same way, flowers of sulphur being used instead of the charcoal. These did not cupel as well as the two preceding determinations and were accompanied by a higher loss of silver; 4.13 per cent and 4.16 per cent respectively.

The three other determinations were treated with lead oxalate, ammonium sulphate, and ammonium acetate respectively. The method of procedure was as follows. The filter containing the silver chloride was partially dried, the chloride moistened

with a saturated solution of the salt used and the whole partially dried again. This operation was repeated three times and the filter thoroughly dried, ignited, and cupelled as before. In this manner the salt is intimately mixed with the silver chloride. All the cupellations proceeded without any spitting. The determination in which lead oxalate was used showed a loss of 5.53 per cent; that in which ammonium sulphate was used, a loss of 5.14 per cent, and that in which ammonium acetate was used, a loss of 3.04 per cent.

Experiment 22. This experiment was carried out for the purpose of determining the use of zinc in the reduction of the silver chloride. In two of the determinations of this series about one half gram of zinc dust was added to the silver chloride after all the nitric acid had been removed by washing by decantation. After mixing well two or three drops of hydrochloric acid were added and the mixture transferred to the filter and washed. The filter and contents were then dried, ignited, and cupelled as before. Too large an excess of zinc was used which prevented good cupellation and hence caused a large loss of silver; 13.1 per cent and 4.31 per cent respectively. The other two determinations of this series were treated the same as the first two with the exception that sufficient acid was added to dissolve all of the zinc. Care was taken not to have much excess

of acid and the solution was diluted after all the zinc had been dissolved in order to precipitate any silver that might have been dissolved by the hydrochloric acid. In this way most if not all of the chloride is reduced before cupellation and very good results were obtained; the loss amounting to 2.17 per cent and 2.6 per cent respectively. These results compare very favorably with two check cupellations with pure silver which were run at the same time and which were accompanied by losses of 2.33 per cent and 1.99 per cent respectively.

Experiment 23. This experiment was carried out for the purpose of testing the method proposed by G. L. Heath[2]. Two grams of test lead were sprinkled over the silver chloride after it had been filtered off and washed. The filters while still wet were placed in hot cupels to which 6 grams of test lead had just been added and were shoved back into the hottest part of the muffle. After the filters had been burned off and the cupels were driving well they were brought forward and the cupellations were completed at a temperature which gave heavy litharge crystals. Two determinations were made by this method and were accompanied by losses of 2.19 per cent and 2.21 per cent respectively. These results compare very favorably with those obtained from the check

determination given above. Mr. Health's method necessitates the use of a very small amount of test lead, and hence reduces the chance for loss of silver by absorption and volatilization. It is also much shorter than the method of reducing the silver chloride with zinc and hydrochloric acid. The results described above are given in the following table for the purpose of better comparison

Results of cupellations of silver chloride.

Experiment number.	Method of Procedure.	Weight of c.p. silver. Gms.		Loss.	Per cent loss.
		Taken.	Found.		
20	Silver cupelled direct	.40041	.39293	.00748	1.87
20	--ditto--------	.39981	.39233	.00748	1.88
20	Silver chloride cupelled direct	.40100	.39130	.00972	2.42
20	Silver chloride cupelled direct	.40110	.36410	.03700	9.22
20	--ditto---------	.40100	.36923	.03177	7.90
21	Char coal added	.39293	.38174	.01119	2.84
21	--ditto--------	.39233	.37925	.01308	3.33
21	Sulphur added	.39130	.37513	.01617	4.13
21	--ditto------	.36923	.35388	.01535	4.16
21	Lead oxalate added	.37925	.35825	.02100	5.53
21	Ammonium sulphate added	.37513	.35583	.01930	5.14
21	Ammonium acetate added	.35388	.34310	.01078	3.04
22	Zinc added	.35825	.31130	.04695	13.1
22	--ditto---	.34310	.32830	.01480	4.31
22	Reduced with zinc	.38774	.37759	.01015	2.60
22	--ditto----------	.40095	.39223	.00872	2.17
23	Cupelled with wet filters	.38356	.37506	.00850	2.21
23	--ditto----------	.39814	.38939	.00875	2.19
23	Silver cupelled direct	.39870	.38940	.00930	2.33
23	--ditto--------	.40313	.39511	.00802	1.99

d. Assay of Copper Matte by the Nitre Method.

These experiments were carried out with the object of obtaining the lead button for the foregoing method by making preliminary fusion to determine the reducing power of the matte and by using nitre in the subsequent fusion. The preliminary fusions were made with the following charge and results.

	Experiment No. 24.	No. 25.
Matte used	4 grams	Duplicate
Soda carbonate	6	
Litharge	50	
Silica	3	
Salt	Cover	
Wt. of lead button	17.0	16.95
Reducing power	4.25	4.24

With this reducing power 1 A. T. of the matte would reduce approximately 124 grams of lead. The nitre used in these experiments had an oxidizing power of 4.0. The charges used and results obtained with the nitre are given in the following table.

Experiment	No. 26.	No. 27.	No. 28.	No. 29.	No. 30.
Matte taken	.5 A. T.	1 A. T.	.5 A. T.	1 A. T.	1 A. T.
Soda carbonate	20 grs.	40 grs.	20 grs.	20 grs.	50 grs.
Borax	10	20	10	20	20
Litharge	150	250	150	250	200
Nitre	9	18	9	20	28
Silica	6	12	6	15	15
Cover	Salt	Salt	Salt	Salt	Salt
Wt. of lead button	28.9	56	23.5	59	13
For cupellation	22.5	13	22.5	20	20
Wt. of Ag	.04430	.09769	.04620	.09510	.09344
Correction	.00067	.00109	.00067	.00109	.00090
Ozs. per ton of Ag	87.26	96.60	91.06	94.01	92.54

In all of the experiments there was considerable tendency for the charge to boil over but with a little attention this was avoided. In every case there was a good clean pour which resulted in a homogeneous red, cuprous oxide slag.

From the results given above it is evident that the nitre slags a considerable amount of the silver with the copper and it will also be noticed that this amount seems to depend on the size of lead button obtained. For in Experiments No. 26, No. 28, and No. 30 where sufficient nitre was used to obtain a

button weighing less than 30 grams the results are lower than those of experiments No. 27 and No. 29 where the lead button weighed over 50 grams.

e. Copper-matte, nitre and sodium peroxide.

In recent years the use of sodium peroxide in analytical chemistry has received considerable attention. It has been found that sodium peroxide can be used to great advantage in many cases where a strong oxidizing agent is needed. For fusing clays and various minerals it far surpasses sodium carbonate or potassium acid sulphate and it is a much stronger oxidizing agent than either nitre or potassium chlorate. The chief advantage of sodium peroxide as a fusion medium is the rapidity with which the fusion is accomplished, this being almost instantaneous.

Due to the fact that sodium peroxide is such a strong oxidizing agent and to the fact that it can be so generally applied in analytical chemistry, it was thought that it might also be profitably substituted for nitre in the assay of certain materials which contain copper, arsenic, antimony, etc. Consequently this set of experiments was carried out for the purpose of investigating the use of sodium peroxide

in the assay of copper mattes;-- its effect on the slagging of the silver, copper, etc.

Before any regular fusions were made several tests were carried out with the object of determining the oxidizing power of the sodium peroxide. These fusions were made with a pyrites ore which was found by the following charge to have a reducing power of 9.92.

Experiment	No. 31.	No. 32.
Ore taken	3 grams	Duplicate
Soda carbonate	6	-----
Litharge	60	-----
Salt	Cover	-----
Wt. of lead button	29.75	29.80
Reducing power	9.91	9.93

The following table gives the charges and results of the experiments to determine the oxidizing power of the sodium peroxide.

Experiment	No. 33.	No. 34.	No. 35.	No. 36.	No. 37.
Wt. of ore taken	3 grams.	3 grams.	3 grams.	3 grams.	3 grams.
Soda carbonate	3	3	3	3	3
Litharge	60	60	60	60	60
Sodium peroxide	3	3	5	5	10
Silica	3	3	3	3	3
Salt	Cover	Cover	Cover	Cover	Cover
Wt. of lead button	28.9	29.2	25.6	25.4	14.1
O. P.	.3	.17	.82	.84	1.56

It will be seen that a constant oxidizing power for sodium peroxide can not be obtained. It is well known that fluxes and temperature have a great influence on the oxidizing power but with these experiments the fluxes are identical with each other and all the fusions were made at the same time and as nearly as possible at the same temperature. Furthermore it will be noticed in the above table and in all subsequent experiments in which sodium peroxide was used that its oxidizing power increases with the amount used. But at no time does it even approximate the value of the oxidizing power of nitre and the following calculations show that the two should be about equal. Two gram molecules or 202 grams of potassium nitrate give three atomic weights or 48 grams of oxygen which can be used for oxidizing purposes, while one gram molecule or 78

grams of sodium peroxide gives one atomic weight or 16 grams of oxygen; that is, 1 gram of nitre gives 48/202 or approximately 1/5 gram of oxygen while 1 gram of sodium peroxide gives 16/78 or approximately 1/5 gram of oxygen.

The low oxidizing power obtained is probably due to the fact that the sodium peroxide attacks the crucible and is partially used in that way and also as explained later to the fact that a large quantity of the copper sulphide seems to be oxidized to the sulphate instead of to the oxide and sulphur dioxide. It was found that because of the low oxidizing power of the sodium peroxide it was impossible to use a sufficient quantity to give a button weighing 30 grams or less, for when more than 40 grams of the peroxide was used, it attacked the crucible so violently that a hole was eaten through the bottom.

Consequently it was decided to use a mixture of sodium peroxide and nitre.

The following tables give the charges used and the results obtained from these experiments.

	Experiment No. 38.	No. 39.	No. 40.	No. 41.
Matte used	1 A. T.	1 A. T.	1 A. T.	1 A. T.
Soda carbonate	30 grs.	50 grs.	50 grs.	50 grs.
Borax	20	20	20	20
Litharge	250	200	200	200
Sodium peroxide	40	25	20	35
Nitre		20	23	18
Silica	15	15	15	15
Cover of salt				
Wt. of lead button	84	33.9	30	31
For cupellation	20	20	20	20
Wt. of Ag	.10104	.10556	.10460	.10586
Correction	.00108	.00090	.00090	.00090
Oz. of Ag per ton	99.96	104.66	103.70	104.96
O. P. of sodium peroxide	1.0	.41	.1	.6

Experiment	No. 42.	No. 43.	No. 44.	No. 45.	No. 46.
Matte used	.5 A. T.	.5 A. T.	.5 A. T.	.5 A. T.	.5 A. T.
Soda carbonate	25 grs.	50 grs.	50 grs.	50 grs.	50 grs.
Borax	12	12	12	12	12
Litharge	110	110	110	110	110
Sodium peroxide	20	20	10	25	15
Nitre	9	7	9	6	8
Silica	10	10	10	10	10
Salt	Cover	Cover	Cover	Cover	Cover
Wt. of lead	20	31	27	30	30
For cupellation	13	16	17	17	18
Wt. of Ag	.05054	.05165	.04990	.05209	.05177
Correction	.00052	.00052	.00052	.00052	.00052
Oz. of Ag per ton	100.04	102.26	98.76	103.08	102.50
O. P. of sodium peroxide	.3	.15	0	.32	0

As seen from the above results a mixture of sodium peroxide and nitre does not slag as much silver as the nitre alone. In all these experiments a good liquid fusion was obtained. However there was considerable difficulty experienced in preventing the fusion from boiling over but this could be done by proper regulation of the heat. It was noticed further that the tendency to boil over decreased as the ratio of the sodium peroxide to the nitre increased, and also that higher results were obtained as this ratio increased. Experiment No. 38 in which no nitre was used gave a very quiet fusion. All the above fusions poured well and gave a red slag showing the presence of cuprous oxide. This red slag was covered with a light blue slag which increased in amount and in intensity of color with the amount of sodium peroxide used. On being tested, this blue slag showed the presence of a large amount of sulphate. From the above facts it was thought that the sodium peroxide was partially used up in oxidizing the copper to copper sulphate. To further investigate this matter, more qualitatively than quantitatively, the following fusions were made.

In one a mixture of sodium peroxide and nitre was used and in the other nitre alone was used. The sulphate in the slags

was determined and the excess of sulphate in the first one over that in the second was ascribed as being due to the oxidizing of the copper sulphide by the sodium peroxide to copper sulphate.

Charges used.

Experiments	No. 47.	No. 48.
Matte used	1 A. T.	1 A. T.
Soda carbonate	50 grs.	50 grs.
Borax	20 grs.	20
Litharge	100	200
Sodium peroxide	20	
Nitre	23	24
Silica	15	15
Salt	Cover	Cover
Wt. of lead button	40	39
Wt. of slag	292	223.5

The slags were ground and passed through a 100 mesh sieve and a 1 gram sample was taken for analysis. This was boiled with 50 c. c. of water and the insoluble residue filtered off and washed with hot water. The sulphate in the filtrate was then determined as $BaSO_4$ and the following results were obtained.

	Experiment No. 47.	No. 48.
Wt. of $BaSO_4$	.0977 grs.	.0790 grs.
Per cent of SO_4 present	4.02	3.25
Wt. of SO_4 in slag	11.74	7.26
Excess of SO_4 due to Na_2O_2	4.5	

Thus it is seen that a considerable amount of the oxygen of the sodium peroxide is used in oxidizing the copper sulphide to the sulphate.

f. Copper matte, using red lead and lead peroxide.

This series of experiments was carried out for the purpose of determining the use in assaying mattes of substances which are at the same time oxidizing agents and sources of supply for the lead.

For this purpose gram molecular weights of red lead and lead peroxide were intimately mixed and the following preliminary fusion was made to determine the oxidizing power of the mixture.

	Experiment No. 49.
Matte used	10 grs.
Soda carbonate	20
Borax	10
Mixture (PbO_2 and Pb_3O_4)	90
Silica	5
Salt	Cover
Wt. of lead button	17
O. P. of the mixture	.28

With this oxidizing power 115 grams of the mixture would give about a 30 gram button when .5 A. T. of the matte was used; hence the following fusion was made with the results shown.

Experiments	No. 50.	No. 51.
Matte used	.5 A. T.	Duplicate
Soda carbonate	50 grs.	
Borax	12	
Mixture	.15	
Silica	10	
Salt	Cover	
Wt. of lead	34	32.3
For cupellation	20	20
Wt. of Ag	.04930	.05065
Ozs. of Ag per ton	98.6	101.30

This charge gave a very good fusion and formed the red cuprous oxide slag. It has an advantage over the nitre method in that there was no tendency to boil over. And by varying the amount of the mixture used or by the addition of argols or some other reducing agent in the case of a matte with a low reducing power no nitre need be used. The results obtained are higher than those from the nitre method.

g. Determination of the Copper Slagged in the Foregoing Experiments.

These determinations were made for the purpose of comparing the per cent of copper slagged by the different methods.

The filtrate from the silver chloride was diluted to one liter and duplicate samples of 25 c. c. each were drawn off by a pipette and run into 2 inch casseroles. To each sample there was added 1 c. c. of concentrated sulphuric acid which was sufficient to precipitate all the lead present and leave a slight excess of the acid. The samples were then evaporated on the hot plate. When the residue had become white, due to the dehydration of the copper sulphate, the casseroles were removed from the hot plate and about 25 c. c. of water added. The solution and residue of copper sulphate were then transferred to a 150 c. c. Erlenmeyer flask and made slightly alkaline with a sodium hydroxide solution. An excess of acetic acid was then added together with 6 c. c. of a potassium iodide solution (2 c. c.   1 gram of KI). The liberated iodine was titrated with a standard sodium thiosulphate solution as described in Miller's Quantitative Analysis for Mining Engineers, p. 90. The thiosulphate solution was standardized against samples of electrolytic

copper. 1 c. c. was found to be equivalent to .00525 grs. of Cu.

The results tabulated below are the average of the duplicates run on each sample. 1 assay ton of the matte contains 16.33 grams of copper.

Experiment	No. 30.	No. 39.	No. 40.	No. 41.
Nitre	28	20	23	18
Sodium peroxide		25	20	35
Grs. of Cu in lead	7.8652	10.4964	9.6776	9.7465
Grs. of Cu slagged	8.4710	5.8398	6.6586	6.5897
Per cent of Cu slagged	51.85	35.75	40.75	40.39

From these results it will be seen that the nitre alone slags more copper than when used in combination with the sodium peroxide, and that the amount of copper slagged when the peroxide is used does not seem to depend on the amount used, for in No. 41 in which 35 grs. of the peroxide was used practically the same per cent is slagged as in No. 40 in which 20 grs. of the peroxide was used,while in No. 39 in which 25 grs. was used 5 per cent less of copper was slagged. It is probable however that factors such as temperature and length of time of fusion influence the amount of copper slagged

to a considerable extent.

The following table gives the amount of copper slagged by the mixture of red lead and lead peroxide. One half assay ton of the matte was used which is equivalent to 8.1681 grs. of copper.

Experiment	No. 50.	No. 51.
Mixture	115	115
Grs. of Cu in lead	4.5939	4.7512
Grs. of Cu slagged	3.5742	3.4169
Per cent of Cu slagged	43.75	41.83

It is seen that while the above mixture does not slag as much copper as the nitre it does slag more than the sodium peroxide and nitre.

h. Comparison of the Results Obtained in the Experiments with the Copper Matte.

In the following table only the highest and most reliable results obtained by each method are given. Results obtained in the assay of copper matte by different methods.

Exp. No.	Method.	Oz. per ton of Ag.	% Cu slagged.
5	Combination	106.03	
7	All-fire	99.9	
8	All-fire	99.4	
15	Nail	102.51	
16	Nail	102.53	
27	Nitre	96.60	
30	Nitre	92.54	51.85
38	Sodium peroxide	99.96	
39	Sodium peroxide and nitre	104.62	35.75
41	--ditto----------------	104.92	40.39
51	Red lead and lead peroxide	101.30	41.83

From the above table it will be seen that while the mixture of sodium peroxide and nitre does not slag as much copper as nitre alone, it does in some way prevent the silver from being slagged and hence gives higher results. A strong oxidizing agent therefore does not necessarily slag off the silver.

i. Assay of copper ore.

These experiments were carried out for the purpose of investigating the application of the new method previously described to copper ores which carried no sulphides. Two series of experiments were carried out; in the first series the ore was assayed by the usual method given on page 119 of Lodge's "Notes on Assaying;" in the second series the method of direct cupellation of the silver chloride was used. The ore for these experiments was made from 55 grams of a Honduras silver ore running about 1000 ounces to the ton and 500 grams of a copper ore which contained about 30 per cent copper. The ore was put through a 100 mesh sieve and well mixed before using. On analysis by the iodide method[10] it was shown to contain 26.95 per cent copper. The charge used and the results obtained from the old method are given in the following table.

Experiment	No. 52.	No. 53.	No. 54.	No. 55.	No. 56.
Ore used	.5 A. T.	Duplicate.	Duplicate.	Duplicate.	Duplicate.
Soda carbonate	15 grs.				
Borax	5				
Litharge	110				
Argols	2 1/2				
Silica	4				
Salt	Cover				
Wt. of lead button	29	30	29.3	28.7	25
Wt. of Ag	.04506	.04304	.04470	.04508	.04072
Correction	.00050	.00050	.00050	.00050	.00050
Oz. per ton of Ag	89.12	85.08	88.40	89.16	80.44

The buttons from No. 52, No. 53, No. 54, and No. 55 were scorified with 20 grams of test lead and a pinch of borax and silica. The buttons resulting from this scorification were fairly free from copper and were cupelled. The button from No. 56 was cupelled directly without any preliminary scorification. There was so much copper in the button, however, that the cupellation had to be carried on at a higher temperature than usual, hence there was a considerable loss of silver as shown.

In the second series of experiments the buttons were obtained by using the same charge as above. The silver chloride was obtained as previously described and was cupelled according to G. L. Health's[2] method.

The following table gives the results obtained by direct cupellation of the silver chloride.

Experiments	No. 57.	No. 58.	No. 59.	No. 60.	No. 61.	No. 62.
Ore used	.5 A. T.	----	----	----	----	----
Soda carbonate	15 grs.	----	----	----	----	----
Borax	5	----	----	----	----	----
Litharge	110	----	----	----	----	----
Argols	2 1/2	----	----	----	----	----
Silica	4	----	----	----	----	----
Salt	Cover	----	----	----	----	----
Wt. of lead	28	28.5	29.2	27.8	28.5	28.5
For cupellation	20	20	20	20	20	20
Wt. of Ag	.04500	.04455	.04496	.04610	.04540	.04530
Correction	.00050	.00050	.00050	.00050	.00050	.00050
Ozs. of Ag per ton	89.00	88.10	88.92	91.20	89.80	89.60

As seen from the table the results check very week among themselves and also agree very closely with the results obtained by the old method. They are even a little higher than the former results. Although the new combination method is no shorter than the old method in the case of this particular ore, it would be considerably shorter with an ore containing sufficient copper to necessitate two or more scorifications. Then too with the combination method all the copper is removed before the cupellation which can therefore be carried on at a

lower temperature and thus the loss by volatilization of the silver is minimized.

k. Experiments to Determine the Influence of Litharge on the Slagging of Copper.

These experiments were carried out for the purpose of determining the amount of copper slagged by different amounts of litharge and the ratio of the copper to the lead in the button. The copper ore previously used was run with the following charge using different amounts of litharge.

Experiment	No. 63.	No. 64.	No. 65.	No. 66.	No. 67.
Ore taken	.5 A. T.	----	----	----	----
Soda carbonate	15	----	----	----	----
Borax	8	----	----	----	----
Litharge	60	75	85	95	110
Iron dust	6	----	----	----	----
Silica	5	----	----	----	----
Salt	Cover	----	----	----	----
Wt. of lead button	22.5	26.5	22.5	31	30
Grs. of Cu in lead button	3.221	3.150	2.751	2.661	1.659
% of Cu in lead button	14.31	11.89	10.00	8.60	5.58
Grs. of Cu slagged	.709	.780	1.179	1.269	2.271
% of Cu slagged	18.02	19.85	30.00	32.28	57.78

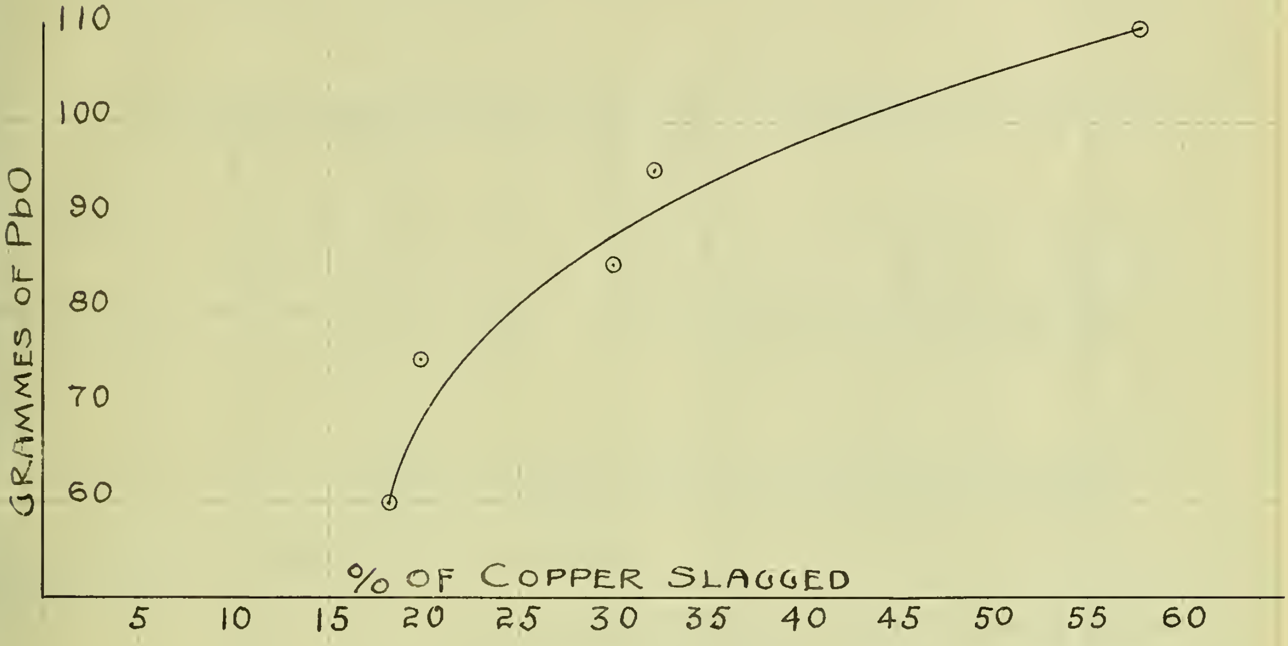
.5 A. T. of ore contains 3.93 grs. of Cu.

In these experiments iron dust was used as the reducing agent and was added after the charge had come to a quiet fusion. The results show that the litharge plays a very

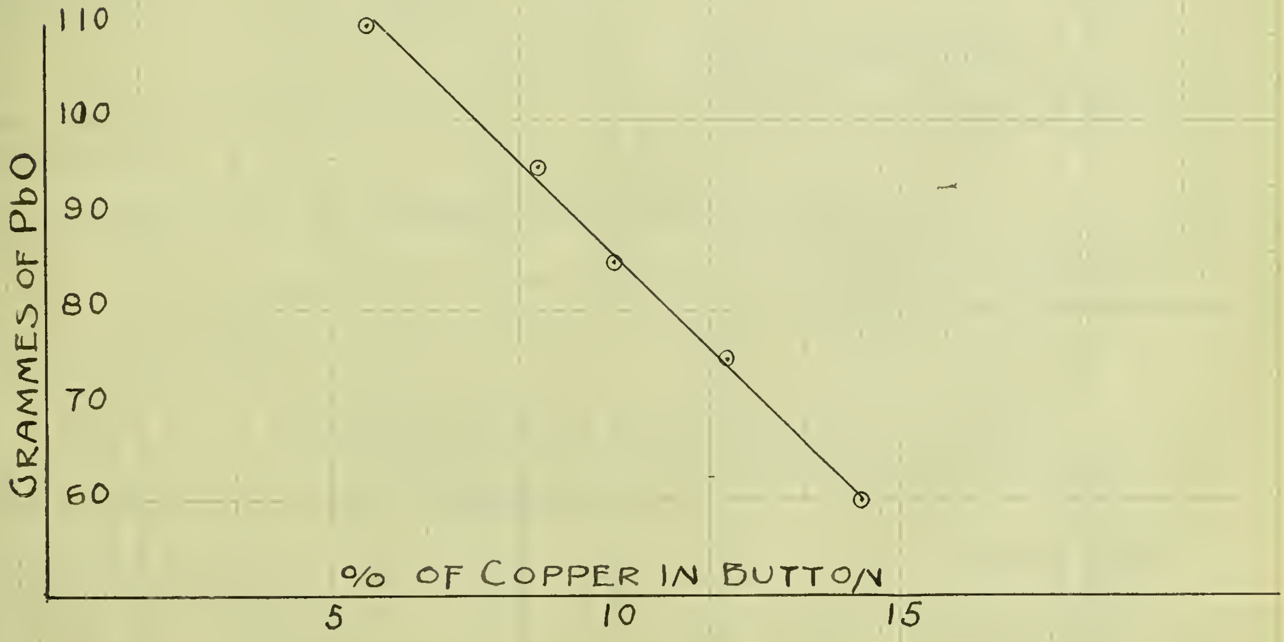
important part in the slagging of copper, which confirms the experiments carried out by Lodge[12]. It also influences the size of the lead button obtained from the fusion.

The accompanying curves show the relation between (1) the per cent of Cu slagged and the amount of litharge used and the relation between the (2) per cent of Cu in the lead button and the litharge.

CURVE SHOWING RELATION BETWEEN AMOUNT OF LITHARGE USED AND % OF COPPER SLAGGED.



CURVE SHOWING RELATION BETWEEN AMOUNT OF LITHARGE USED AND % COPPER IN LEAD BUTTON



III. CONCLUSIONS.

From the experimental work done in these investigations the following conclusions may be drawn:--

1. The old combination method for the assay of copper mattes will give higher results than any other method now in use.

2. The all-fire method gives results considerably lower than the combination method.

3. The nail method in combination with the new method of direct cupellation of the silver chloride does not give as high results as the combination wet and dry method~~s~~, but does give higher results than the all-fire method and is much shorter and easier to carry through than either of the others.

4. That G. L. Heath's[2] method for the direct cupellation of silver chloride is the shortest and gives the best results of all methods experimented with.

5. The use of nitre causes a considerable loss of silver probably due to its being slagged with the copper.

6. The use of sodium peroxide with the nitre in some way prevents the loss of the silver and hence gives results that are considerably higher than those obtained when nitre is used alone. On the other hand there is not so much

copper slagged when the sodium peroxide is used but as the copper is readily removed by solution this is no particular disadvantage. The results obtained when the peroxide was used compare more favorably with the results from the old combination method than do the results obtained from any other methods tried.

7. It is impossible to obtain a value for the oxidizing power of sodium peroxide that will approach the theoretical value. This is probably due to the fact that some of the peroxide is used up in oxidizing the copper sulphide to copper sulphate and in attacking the crucible in which the fusion is made and also to other factors such as temperature, time of fusion, etc.

8. Red lead, lead peroxide, or a mixture of the two may be substituted for litharge and the oxidizing agent in the assay of mattes with fairly satisfactory results.

9. The new method when applied to a silicious copper ore gives results that compare very favorably with results obtained by the old all-fire method. It gets rid of all the copper before cupellation, so that this operation can be carried on to better advantage.

10. The amount of copper slagged increases with the amount of litharge present, other fluxes remaining the same. This

confirms the results obtained by R. W. Lodge[12].

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